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# ZIRCONIUM ABUNDANCES IN METEORITES
# AND IMPLICATIONS TO NUCLEOSYNTHESIS

by

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## ABSTRACT

The atomic abundance of Zr has been established at $16 \pm 5$ Zr atoms/$10^6$ Si atoms in seventeen ordinary chondrites, which agrees well with Aller's (1962) solar value of 14 Zr atoms/$10^6$ Si atoms. Apparently, fractionation of Zr has occurred within the chondritic family, since $22 \pm 3$ Zr atoms/$10^6$ Si atoms were observed in seven Type II and Type III carbonaceous chondrites. Zr has been enriched in four Ca-rich achondrites by a factor of five, which is consistent with other trace-element enrichments. Zr may be depleted in Ca-poor achondrites and pallasitic olivines. The low Zr abundance in chondrites, coupled with Rb, Sr, Y, and Mo chondritic abundances, indicates ~50% enhancement of the odd-A mass distribution at A = 89 due to the 50-neutron-shell closure. Abundance values of Zr and other nearby elements indicate $Fe^{56}$ seed nuclei were exposed to different neutron fluxes. The atomic ratio Zr/Hf of 100 in meteorites compared with 106 in the terrestrial crust indicates no serious fractionation between these two very similar chemical elements.

# INTRODUCTION

In order to establish a "cosmic" elemental abundance distribution that will be considered reliable for comparison against nucleosynthetic theories, abundances of the chemical elements must be accurately ascertained. Chondritic meteorites have been considered to represent the closest approach to nonvolatile primordial matter, as indicated by Suess and Urey (1956). Their choice has been more firmly corroborated by the observation that no internal fractionation exists in the relative abundances of the fourteen rare-earth elements in all chondritic categories, as found by Schmitt et al. (1963a, 1964).

When Suess and Urey (1956) compiled the elemental abundances, the abundances of zirconium and hafnium were not well known. The zirconium value of Pinson et al. (1953) was assumed valid. For the hafnium abundances, Suess and Urey assumed that the atomic Zr/Hf ratio of 110 found in a wide variety of terrestrial minerals by Hevesy and Würstlin (1934) should be nearly identical to that found in chondritic meteorites. This paper corroborates their assumption.

Accurate abundance values of zirconium are desirable for a number of reasons. One of the nuclides of zirconium, $Zr^{90}$, has 40 protons and 50 neutrons. Fifty neutrons, constituting a closed nuclear shell, are responsible for closed-shell "magic" nuclear properties such as low neutron capture cross sections (Clayton et al., 1961, Fig. 9). Therefore, in any nucleosynthetic model involving neutron captures, the zirconium abundances will most certainly be greatly affected and zirconium abundances must be accurately established, at least to a better degree than the anticipated phenomena, in order to allow a reliable comparison with theory.

A second reason for desiring accurate abundance values of zirconium concerns the prior allusion to the critical Zr/Hf ratio, which fluctuates

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within a rather narrow range (factor of two) in terrestrial matter. If
meteoritic and terrestrial matter had a common origin, it may be predicted
that the Zr/Hf ratio in chondritic meteorites should be nearly identical to
that in terrestrial matter. Since these two elements have nearly identical
geochemical properties (Goldschmidt, 1954) because of their tetravalent
oxidation state and nearly identical ionic radii (Zr 0.87 $\overset{o}{A}$, and Hf 0.86 $\overset{o}{A}$),
identical Zr/Hf ratios in chondritic meteorites and terrestrial matter would
again strengthen the primordiality arguments for nonvolatile chemical
elements and the hypothesis of common origin of chondritic and terrestrial
matter.

To establish the "cosmic" abundance distribution, the abundances
of trace elements must be determined in all meteoritic categories--achondritic
and pallasitic, etc., as well as chondritic. For example, if a given trace
lithophilic element were deficient in Ca-rich achondrites compared with
chondrites, the interpretation of the chondritic abundance must be critically
evaluated in terms of an over-all meteoritic model. In the past, only a
few trace elements, viz., the fourteen rare-earth elements (Schmitt et al.,
1963a, 1964) and cadmium (Schmitt et al., 1963b), have been determined
in many meteorites from all chondritic categories. Accurate zirconium
abundances within the meteoritic family, therefore, will enhance our
understanding of the family and its problems.

## EXPERIMENTAL

Abundances of zirconium were determined in 37 meteorites and four
terrestrial basalts by ES (emission spectroscopy) at the California Institute
of Technology spectroscopic laboratory by Bingham and Chodos, and by
NAA (neutron activation analysis) at the General Atomic laboratory in
four chondritic meteorites by Schmitt (1962). The complete experimental
methods for both techniques are given in the Appendix.

# RESULTS AND DISCUSSION

## Results of ES and NAA

Es and NAA results have been compiled in Table 1. In column four, the average values of the abundances in the previous column are given, with the (±) values indicating the mean deviation. The last column lists the atomic abundance of Zr relative to $10^6$ Si atoms, the chosen standard in elemental abundances.

The first series of ES abundances are listed in Table 2; the average of the best analyses from Table 2 (group C) have been included in Table 1 and also in the averages of column four of Table 1.

Of all the Zr abundances determined by ES, those determined during the first series, on December 6, 1963 (Table 2), and the second series, on February 11, 1964, are considered least accurate; i.e., Zr abundances of less than 10 ppm were borderline plate readings and could be 10 ppm or less. The Zr values determined by ES on the last of the three measurement dates (March 19, 1964) are designated by $\underline{c}$ in Table 1 and are considered quite accurate. In short, these improved ES analyses may be attributed to better film and line reading experience (see the Appendix for details).

Since the Zr abundances in Ca-rich achondrites are in the 60 ppm range, no experimental difficulty was encountered in their analyses in the second series of ES runs, labelled $\underline{d}$ in Table 1.

Zirconium abundances in two Ca-poor enstatitic achondrites and two samples of olivine from pallasites were determined by ES during the second series; therefore, the reliability of the Zr abundances at 7 ± 1 ppm in Ca-poor achondrites and 5 ± 2 ppm in pallasitic olivines should be treated with caution in interpretation. In these meteoritic categories, Zr is certainly less than 10 ppm.

Four terrestrial basalt Zr abundances average 180 ± 40 ppm and agree well with the basalt average of 150 ppm by Chao and Fleischer (1960).

Table 1

ABUNDANCES OF Zr IN METEORITIC AND TERRESTRIAL MATTER BY EMISSION SPECTROSCOPY

| | | Abundances (ppm) | Average Abundances (ppm)[a] | Zr atoms/$10^6$ Si atoms[b] |
|---|---|---|---|---|
| **METEORITE TYPE** | | | | |
| *Chondrites* | | | | |
| Type I carbonaceous | Orgueil | 11 ± 1[c] | 11 ± 1 | 32 ± 3 |
| Type II carbonaceous | Boriskino | 14, 8[c] | 11 ± 3 | 26 ± 7 ⎤ |
| | Cold Bokkeveld | 9, 9[c] | 9 ± 1 | 22 ± 3 ⎮ 23 ± 3 |
| | Mighei | 9, 12[d] | 11 ± 2 | 26 ± 5 ⎮ Avg. |
| | Murray | 7, 9[d]      (13 ± 2)[e] | 8 ± 1 | 18 ± 2 ⎦ |
| | | | 10 ± 1 Avg. | |
| Type III carbonaceous | Felix | 9, 8[c] | 9 ± 1 | 17 ± 2 ⎤ 20 ± 3 |
| | Groznaia | 9, 9[c] | 9 ± 1 | 19 ± 2 ⎮ Avg |
| | Mokoia | 6, 11, 16, 13[d] | 12 ± 3 | 24 ± 6 ⎦ |
| | | | 10 ± 1 Avg. | |
| Enstatite | Abee | 16, 12[c] | 14 ± 2 | 24 ± 3 |
| H-group | Allegan | 10, 6[c] | 8 ± 2 | |
| | Breitscheid | 6, 8[c] | 7 ± 1 | |
| | Ehole | 5, 8[d] | 7 ± 2 | |
| | Hugoton | 6, 9[c] | 8 ± 2 | |
| | Miller | <3, 3[d] [5][f]   (14 ± 3)[e] | 4 ± 1 | 14 ± 1  Avg. |
| | Ochansk | <3, 5[d] [7][f] | 5 ± 2 | |
| | Pantar II | 7, 9[c] | 8 ± 1 | |
| | Potter | 9, 11[c] | 10 ± 1 | |
| | Pultusk | 9, 10[c] | 10 ± 1 | |
| | Tulia | 6, 10[c] | 8 ± 2 | |
| | | | 8 ± 2 Avg. | |
| L-group | Harleton | 8, 12[c] | 10 ± 2 | |
| | Leedy | 3, 6[d] [12][f] | 8 ± 4 | |
| | Mocs | 10, 14[c] | 12 ± 2 | |
| | Modoc | <3, 3[d] [5][f]   (12 ± 1)[e] | 4 ± 1 | 18 ± 6  Avg. |
| | Paragould | 14, 7, 8, 10[d] | 10 ± 2 | |
| | Peace River | 14, 10, 14[d] | 13 ± 2 | |
| | Walters | 21, 17[d] | 19 ± 2 | |
| | (Kyushu) | (13 ± 1)[e] | | |
| | | | 11 ± 4 Avg. | |
| LL-group | Manbhoom | 6, 3[d] [7][f] | 6 ± 2 | 16 ± 7  Avg. |
| | Vavilovka | 12, 14[c] | 13 ± 1 | |
| | | | 10 ± 4 Avg. | |
| **Achondrites** | | | | |
| Ca-rich | Juvinas | 49, 56, 45, 62[d] | 53 | |
| | Moore County | 9, 20, 19[d] | 16 (out)[g] | |
| | Nuevo Laredo | 64, 69[d] | 67 | 81 ± 11[h] Avg. |
| | Petersburg | 50, 50[d] | 50 | |
| | Stannern | 69, 71[d] | 70 | |
| | | | 60 ± 8 Avg. | |
| Ca-poor | Norton County | 9, 6[d] | 8 | |
| | Pena Blanca Springs | 7, 5[d] | 6 | |
| Pallasitic Olivines | Brenham | 3, 3[d] | 3 | |
| | Marjahlti | 6, 7[d] | 6 | |
| **TERRESTRIAL BASALTS** | Columbia Plateau | | | |
| | Miocene    1-300 | 255, 190[d] | 210 ± 20 | |
| | Kilauea    Iki-22 | 210, 180[d] | 200 ± 20 | |
| | Mid-Atlantic GE-159 | 150, 90, 115, 100[d] | 110 ± 20 | |
| | Mid-Atlantic GE-260 | 210, 200[d] | 210 ± 10 | |

[a]Abundances are averages of this paper and of values in brackets of preceding column   Neutron activation values, given in parentheses, have not been included in averages.

[b]Average atomic ratios for H- and L-group chondrites calculated using Urey and Craig (1953) average Si values of 16.9% and 18.5% for the H- and L-group chondrites, respectively.  Si abundances of Mason (1962-1963) and Mason and Wiik (1964) used for other atomic ratios.

[c]These abundances were run against Juvinas as a reference (see text) on March 19, 1964.  Juvinas found at 42, 41, 54, and 45 ppm on that day.

[d]These abundances were run against a sodium carbonate-quartz-carbon standard dilution on February 11, 1964.

[e]Abundances in parentheses are neutron activation results of Schmitt (1962).

[f]Abundances in brackets are averages of group C of Table 2.  These were run on December 6, 1963.

[g](Out) value is not included in average.

[h]Average atomic ratio  was calculated by using $SiO_2$ value of 48.7% for Ca-rich achondrites as given by Urey and Craig (1953).

Table 2

## FIRST ABUNDANCE RUNS OF Zr IN SIX METEORITES BY EMISSION SPECTROSCOPY[a]

| Type of Meteorite | Meteorite | Abundances[b] (ppm) | | |
| --- | --- | --- | --- | --- |
| | | Group A | Group B | Group C (Best) |
| H-group chondrite | Miller | 4, 5, 6 | 3, 6, 10 | 6, 5 |
| | Ochansk | 3, 5, 4 | ----- | 7, 8 |
| L-group chondrite | Leedy | 5, 7, 5 | 6, 5, 3 | 14, 10 |
| | Modoc | 9, 9, 6 | 6, 7, 5 | 5, 6 |
| LL-group chondrite | Manbhoom | 7, 8, 7 | 3, 4, 4 | 7, 8 |
| Ca-rich achondrite | Juvinas | 41, 42, 39 41, 34, 46 | 58, 44, 43 | ----- |

[a]These abundances were run against various standards on December 6, 1963.

[b]Abundance of group A against rock standards; group B against a standard composite of standard granite diluted with quartz (Zr in Zirons); and group C against a combination of G-1 standards and Juvinas. Dilutions of A, B, and C are different.

Abundances for Zr were determined in three identical chondritic meteorites by both NAA and ES. The NAA results are given in parentheses in column 3 of Table 1. The NAA limits stated are one standard deviation due to counting statistics. For Murray, the average 8 ± 1 ppm by ES is less than the 13 ± 2 ppm by NAA, but certainly within the 95% confidence limit. For Miller and Modoc, the NAA results are above the ES results, but, as mentioned above, the ES abundances below 10 ppm determined during the first and second series may be as great as 10 ppm.

It must be emphasized, however, that the NAA results may in fact all be consistently high. Very briefly, the NAA results of this work are based on counting the decay of the equilibrium gamma-ray spectra (with a broad single-channel scintillation spectrometer) of 17-hr $Zr^{97}$, 1-min $Nb^{97m}$, 74-min $Nb^{97}$. Although the radiochemical procedure was quite exhaustive (see Appendix for details) some 15-hr $Na^{24}$ may be present as a possible contaminant. The approximate products of atomic isotopic abundance times the neutron capture cross section in chondrites are ~2000 for $Na^{24}$ and ~0.04 for $Zr^{97}$-$Nb^{97}$ equilibrium production. Since the $Na^{24}/Zr^{97}$-$Nb^{97}$ radioactivity ratio is ~5 × $10^4$, the possible incomplete decontamination (many precipitates were quite bulky) could easily introduce a spurious $Na^{24}$ contribution due to the $Na^{24}$ Compton continuum. In any case, note in Table 1 that the Zr values obtained by NAA of this work overlap the ES values obtained during the last, or third, ES series-- labelled c. Because of the possible Na contamination in the NAA procedure, these NAA values have not been included in the averages. However, the NAA values represent either valid abundances or true upper limits (in case of contamination).

## Comparison of Zr abundance results with other studies

Table 3 lists Zr abundances of meteorites studied in this work and by others. In general, Zr abundances of this work are ~4 times less compared with NAA results obtained by Ehmann and Setser (1963) and

Table 3

COMPARISON OF Zr ABUNDANCES IN INDIVIDUAL METEORITES

| Meteorite | Zr (ppm) | | |
|---|---|---|---|
| | This Work (ES) | Ehman and Setser (1963, 1964) (NAA) | Pinson (1953) (ES) |
| Chondrites | | | |
| Carbonaceous | | | |
| Orgueil | 11 ● 1 | -- | <1 |
| Mighei | 11 ± 2 | 46 | -- |
| Murray | 8 ± 1 | 42 | -- |
| Enstatitic | | | |
| Abee | 14 ± 2 | 35 | -- |
| Ordinary | | | |
| Pultusk | 10 ± 1 | 37 | 32 |
| Harleton | 10 ± 2 | 41 | -- |
| Mocs | 12 ± 2 | 28 | 29 |
| Achondrites | | | |
| Norton County | 8 ± 2 | 22 | -- |

Setser and Ehmann (1964), and ES work by Pinson et al. (1953). Note that Pinson et al. find <1 ppm Zr in the Type I carbonaceous chondrite Orgueil compared with 11 ± 1 ppm as found in this work.

In Table 4, average abundances of Zr in meteorites from all sources to date have been compared. Note that the Zr abundances of ~35 ppm have been found by three different investigations, using two different techniques, while an average abundance of 10 ppm has been found recently by three techniques. Each method will be dealt with to some extent.

Hevesy and Würstlin (1934), first to determine Zr by X-ray spectrography, found a large variation for the Zr abundance. Almost all initial abundance studies of trace elements in chondrites have shown a large spread and, in general, the first abundance determinations were usually high. We do not consider these values to be reliable.

Pinson et al. (1953) using ES technique found 33 ± 8 ppm Zr in 21 "ordinary" chondrites. The values for zirconium in chondrites reported in this paper are considerably lower than those reported by Pinson et al. (1953). The difference in the values is almost certainly due entirely to the choice of analytical line used for zirconium. Pinson et al. do not specifically mention the analytical line used but refer to the work of Pinson (1951) and of Ahrens (1951) for details. Pinson (1951) states that Zr 3391.98 was the analytical line used, whereas we used Zr 3273.05. Zr 3391.98 has an interference from an iron line, Fe 3392.01. In chondritic samples high in iron, the contribution of the iron interference to the zirconium value is considerable, up to 80% in some cases. This is illustrated in Table 5, where a comparison is made between the values for zirconium obtained from the two analytical lines and the relative intensity (in arbitrary units) of an iron line in the same samples. All values are from a single plate. It is apparent that the values of Zr 3391.98 are affected by variations in iron concentration in the samples. Standards and rocks of very low iron concentration would be unaffected. Pinson subtracted

Table 4

COMPARISON OF Zr ABUNDANCES IN METEORITES

| Type of Meteorite | Zr (ppm) | Method[a] | Source |
|---|---|---|---|
| 6 Chondrites | 30 to 160 | X-ray | Hevesy and Würstlin (1933) |
| 21 Ordinary chondrites | 33 ± 8 | ES | Pinson et al. (1953) |
| 5 Ordinary chondrites | 33 ± 7 | NAA (via $Zr^{95}$) | Merz (1962) |
| 12 Ordinary chondrites | 35 ± 4 | NAA (via $Zr^{95}$) | Setser and Ehmann (1964) |
| 3 Ordinary and 1 Carbonaceous chondrites | 13 ± 1 | NAA (via $Zr^{97}$-$Nb^{97}$ equil.) | Schmitt (1962) |
| 8 Chondrites | 10 | X-ray | Erlank (1964) |
| 8 Carbonaceous chondrites | 10 ± 1 | ES | This work |
| 17 Ordinary chondrites | 9 ± 3 | ES | This work |

[a]X-ray = X-ray fluorescence
ES = emission spectrographic.
NAA = neutron activation analysis

Table 5

ES ABUNDANCES OF Zr VIA TWO LINES

| Meteorite | Zr (ppm) 3273.05[a] | Zr (ppm) 3391.98[b] | Fe Relative Intensity 3268.24 |
|---|---|---|---|
| Chondrites | | | |
| Type I carbonaceous | | | |
| Orgueil | 11 | 20 | 90 |
| "Ordinary" | | | |
| Allegan | 10 | 70 | 270 |
| Harleton | 8 | 74 | 305 |
| Enstatitic | | | |
| Abee | 12 | 105 | 420 |
| Achondrite | | | |
| Ca-rich | | | |
| Juvinas | 45 | 73 | 190 |
| Terrestrial Basalt | | | |
| G-1 | 210 | 190 | ~5 |

[a]The 3273.05 Zr line was used to obtain all Zr abundances of this work.

[b]The Fe line at 3392.01 overlaps this Zr line.

an estimated 20% iron contribution from the composite Zr and Fe lines at 3391.98 and 3392.01, and determined the Zr content in meteorites by visual comparison with G-1 and W-1, without the aid of a working curve (Erlank, 1964). Because of Fe interference, the Pinson et al. (1953) Zr abundance values have been discarded; Erlank and Willis (1964) arrived at the same conclusion.

In addition to Zr, Pinson et al. (1953) measured Li, Sc, Sr, Ba, K, and Rb. The Pinson et al. abundance values for Sc, Ba, and Rb at 6 ppm, 8 ppm, and 9 ppm, respectively, are also in serious error compared with the NAA results of 9 ppm Sc by Schmitt et al. (1963a, 1964), 3.5 ppm Ba by Reed et al. (1960), and 2.5 ppm Rb by Smales et al. (1964). (Smales et al. found excellent agreement for Rb abundances between NAA methods and isotopic dilution techniques.) Thus, the validity of the Pinson et al. results appears to be open to question.

Merz (1962), Ehmann and Setser (1963), and Setser and Ehmann (1964), using NAA and radiochemical techniques, determined Zr abundance at 33 ppm via the long-lived 65-d $Zr^{95}$. Merz states that $Zr^{95}$ was isolated and counted via the 0.76-Mev gamma-ray of $Zr^{95}$. However, Merz omits the fact that $Zr^{95}$ has two gamma-rays of 0.72 and 0.76 Mev about equally abundant, and neither Merz nor Setser and Ehmann account for the 90-hr $Nb^{95m}$ (2% of decays) and 35-d $Nb^{95}$ (98% of decays) which are radio-daughters of 65-d $Zr^{95}$ (Strominger et al., 1958). The principal daughter, 35-d $Nb^{95}$, has a 0.765-Mev gamma-ray, ∼100% abundant.

A comparison of the Merz (1962) and Setser and Ehmann (1964) procedures shows that the latter was much more exhaustive. However, in $Ba(Zr, Hf)F_6$ precipitations (which both groups used), 65-d $Zr^{95}$ is decontaminated from the 35-d $Nb^{95}$ daughter. Hume (1951) observed that only ∼0.2% Nb (Nb was present in carrier-free tracer quantities) was coprecipitated with three $BaZrF_6$ precipitations. Also, in the Setser and Ehmann procedure, the final Zr mandelate precipitate decontaminates and separates Nb from Zr (Steinberg, 1960). Consequently, since no 35-d $Nb^{95}$

growth was observed by Setser and Ehmann (1964) while following the $Zr^{95}$ decay, severe contamination must have masked the $Nb^{95}$ growth; this unknown contamination(s) does not necessarily imply an equivalent of 20 ppm contaminant(s), for the following reason. If the neutron capture cross section of contaminant(s) were 1 barn (the $Zr^{94}$ capture cross section is very low at ~0.07 barn) with comparable isotopic abundance, only ~2 ppm of contaminant(s) will mask the 35-d $Nb^{95}$ growth. Merz (1962) does not mention any decay measurements of $Zr^{95}$, so it is not possible to determine whether he could have observed the growth of the $Nb^{95}$ daughter.

Whenever long-lived radionuclides are radiochemically prepared, recycling to constant specific activity should be done to ensure freedom from other contaminating radionuclides, especially in the case of Zr, which has a very low neutron capture cross section of 0.07 barn for $Zr^{94}$ and has a 17.4% isotopic abundance. A search through Slater's (1962) gamma-ray radionuclides reveals at least five long-lived species (61-d $Sb^{124}$, 94-d $Os^{185}$, 34-d $Te^{129m}$, 50-d $In^{114m}$, and 74-d $Ir^{192}$) with half lives between 34 and 94 days and gamma-rays between 0.71 and 0.79 Mev, all of which could be included within the spectrometer resolution. The specificity for the radiochemical decontamination of all of these elements had not been specially checked. Other sources of errors may be possible, such as hydrolysis of reference standard solutions without the proper acid or fluoride normalities.

Inconsistencies between the Merz (1962) and Setser and Ehmann (1964) data exist for the abundances in chondrites, with Merz's Hf at 1.4 ppm and Setser and Ehmann's at 0.20 ppm. Setser and Ehmann chemically separated Hf and Zr (Merz did not) and their Hf abundance of 0.20 ppm appears valid for several reasons. $Hf^{180}$, 35.2% isotopic abundance, has a large neutron capture cross section of 10 barns and no radiodaughters for possible complications. A $_{72}Hf$ abundance of about 0.16 ppm would be predicted by extrapolation of the abundances of the two preceding even-atomic-numbered rare-earth elements, $_{68}Er$ at 0.21 ppm and $_{70}Yb$ at

0.18 ppm, determined in 12 chondrites by Schmitt et al. (1963a). Further-more, Clayton and Fowler (1961) have calculated the absolute Hf atomic abundance at 0.24, which is 50% higher than the Setser and Ehmann Hf atomic value of 0.16 relative to $10^6$ Si atoms.

Calculation of the Hf abundance by Merz involved subtraction of the $Zr^{95}$ gamma-ray contribution. The large Merz (1962) Hf abundance of 1.4 ppm and his omission of the $Nb^{95}$ daughter of $Zr^{95}$ would tend to invalidate the Merz Zr abundance at 33 ppm. On the other hand, the agreement between the observed and predicted Hf abundance by Setser and Ehmann (1964) almost forces an acceptance of their Hf value at 0.20 ppm. It should be noted that for almost all cases of chondritic abundance deter-minations, the most recent and lower values have generally been the true abundances. Finally, the omission of the $Nb^{95}$ daughters by Setser and Ehmann tends to force one to discard their Zr abundance value. The agreement between the Merz, Pinson et al., and Setser and Ehmann Zr abundance at ~33 ppm may possibly be regarded as fortuitous. (The NAA abundance determination of Zr in a few chondrites via the equilibrium of $Zr^{95}$-$Nb^{95}$ is being planned.)

Erlank and Willis (1964) has recently used X-ray fluorescence to determine Zr in meteorites (Table 4). He prepared Zr standards of 10 and 33 ppm using an artificial chondritic base to dilute W-1 and specpure $ZrO_2$. Intensities of the X-ray fluorescence from 8 chondrites were indistinguishable from the 10 ppm standards. The confirmation by Erlank and Willis' X-ray fluorescence results establishes the Zr abundance at 10 ppm.

Implications of Zr atomic abundances to nucleosynthesis

In Table 6, the atomic abundance (via ES of this work) of Zr relative to $10^6$ Si atoms at 16 ± 5 in seventeen ordinary chondrites agrees well with Aller's (1962) solar abundance of 14. (The previous solar abundance (Goldberg et al., 1960) of 5 Zr/$10^6$ Si atoms had been based on older

Table 6

ATOMIC ABUNDANCES OF Zr ATOMS PER $10^6$ Si ATOMS

| Source | Atomic Abundance |
|---|---|
| This work (17 ordinary chondrites) . . . . . . . . . . . . . . . . . . | $16 \pm 5$ |
| (7 Types II and III carbonaceous chondrites) . . . . . . . | $22 \pm 4$ |
| Aller (1962) (Solar abundance) . . . . . . . . . . . . . . . . . . . . | 14 |
| Suess and Urey (1956) . . . . . . . . . . . . . . . . . . . . . . . . . | 55 |
| Clayton and Fowler (1961) . . . . . . . . . . . . . . . . . . . . . . | 40 |
| Cameron (1963) . . . . . . . . . . . . . . . . . . . . . . . . . . . . . | 23 |

f-values.) The Zr atomic value at 22 ± 4 is 40% higher in seven Type II and Type III carbonaceous chondrites compared with ordinary chondrites, but overlaps the ordinary chondritic abundance within the 67% confidence level. These observed meteoritic abundances have been compared against the Suess-Urey (1956), Clayton and Fowler (1961), and Cameron (1962-1963) values. Values of Suess-Urey and Cameron are largely based on the best estimates of a smooth abundance curve, while the Clayton and Fowler (1961) and Clayton et al. (1961) abundances rest largely on detailed theoretical treatment of two principal contributions for element nucleosynthesis, namely, the s-process, or slow-neutron capture, and the r-process, or rapid-neutron capture.

In Fig. 1, the atomic abundance in Type I carbonaceous (Orgueil and Ivuna) and "ordinary" chondrites for the odd-masses (85 through 95) have been plotted from the elemental abundances of Rb by Smales et al. (1964), Rb and Sr by Smales et al. (1964) and Murthy (1964), Y by Schmitt et al. (1963a, 1964), and Mo by Kuroda and Sandell (1954). Theoretical abundances($\times$) and (o) values, by Clayton and Fowler (1961) and Cameron (1962-1963), respectively, have been included.

The first noteworthy feature that may be noted from Fig. 1 concerns the relatively higher displacement of the odd-A abundance curve for the Type I carbonaceous chondrites. A peak at A = 89, well defined in both curves, probably represents the enhancement of abundances at the 50-neutron shell due to the s-process. The magic 50-neutron shell seems to be responsible for an ~50% enhancement above a straight line drawn from A = 87 to A = 95 in "ordinary" chondrites. The carbonaceous chondrites apparently show the same enhancement; Mo abundance in these chondrites must be determined to check this point. Since the over-all chemical properties of these five elements (Rb, Sr, Y, Zr, and Mo) are distinctly different, the relative displacement of the two experimental curves indicates no serious fractionation between Type I carbonaceous and "ordinary" chondrites. This observation is important if Type I carbonaceous chondrites
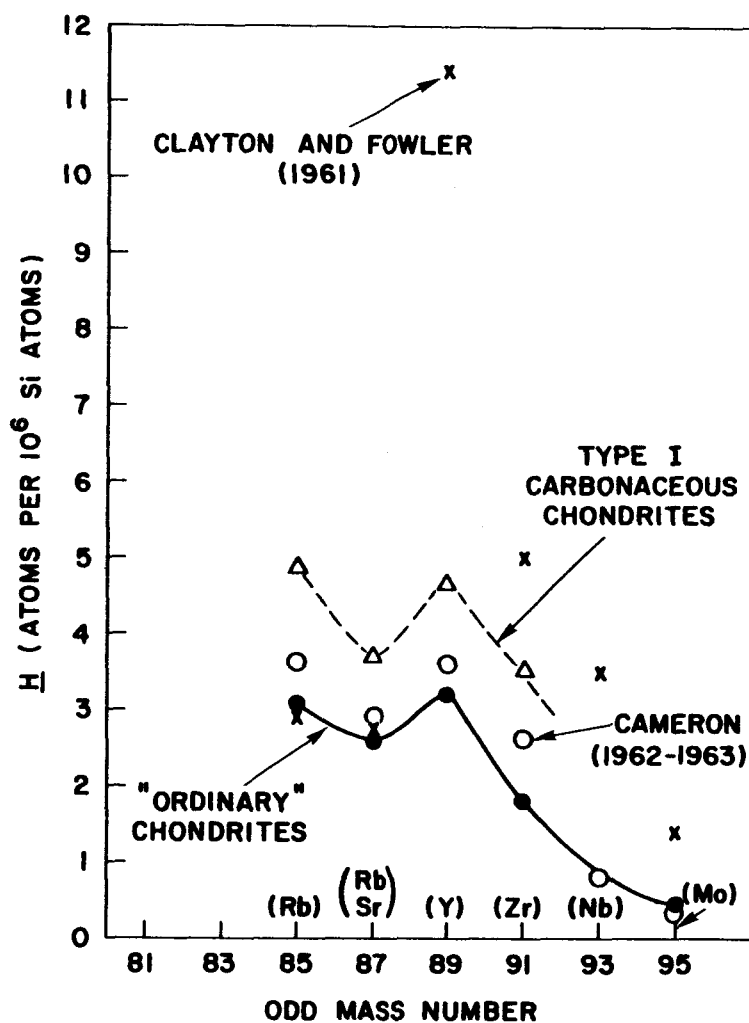
Fig. 1. Abundances of odd mass numbers from 85 through 95. Ordinary chondritic abundances of Rb, Sr, Y, and Mo are from Urey (1964), and Zr is from this work. Type I carbonaceous chondritic abundances used were: Rb average by Murthy (1964) in Orgueil, and Smales et al. (1964) in Ivuna; Sr by Murthy (1964) in Orgueil; Y by Schmitt et al. (1963a, 1964); and Zr of this work.

are considered the closest approach to primordial matter in view of their high abundances of rare gases and chalcophilic elements, etc. Closer inspection reveals a possible 15% depletion of Rb in "ordinary" chondrites relative to Type I carbonaceous chondrites.

Theoretical analysis by Clayton et al. (1961) and Clayton and Fowler (1961) predicts a peak at A = 89, about 3.6 times higher than the peak in "ordinary" chondrites. Note that the theoretical values at A = 85 and 87 closely match the observed "ordinary" chondritic values. In the theoretical calculations, the $\sigma$N curve (Fig. 20 of the Clayton et al., 1961, paper) was assumed to be smooth and was based on a few 25-keV neutron cross sections and some measured abundance data. In the vicinity of Zr, and from Hf through Au, the observed Suess-Urey (1956) abundances were lowered by a factor of 2.5.

Calculated atomic abundances for Y and Zr primarily result from a buildup of $Y^{89}$ and $Zr^{90}$ due to the s-process at the 50-neutron-shell closure. Capture cross sections for 30 keV neutrons were measured at ORNL (see Clayton et al., 1961) only for $_{37}Rb^{87}$ and $_{40}Zr^{90}$ (both having 50 neutrons) at 75 and 13 mb, respectively. Interpolation of the above data and smooth cross-section criteria yielded cross sections of 16 mb for $_{38}Sr^{88}$ and 18 mb for $_{39}Y^{89}$. Capture cross sections for other isotopes of these elements were generally from 5 to 10 times larger. In order to bring the theoretical values in line with the observed abundances, the ~30 keV neutron capture cross sections for the 50-neutron-shell isotopes must be increased by a factor of about four.

On the other hand, Clayton et al. (1961) have calculated a super-position of different neutron exposures of iron (the $Fe^{56}$ atoms are assumed to be the initial seed nuclei) in order to fit the observed $\sigma$N curve. Figure 2 is a reproduction of Fig. 19 of Clayton et al. (1961). Note that at A = 88, the calculated $\sigma$N curve drops precipitously before resuming a nearly constant slope at A = 95. The equation for the calculated curve is given (Clayton et al., 1961) as $\sigma_A N_A = 2160 \ \psi(n_c = 2.8) + 990 \ \psi(n_c = 6.9) +$
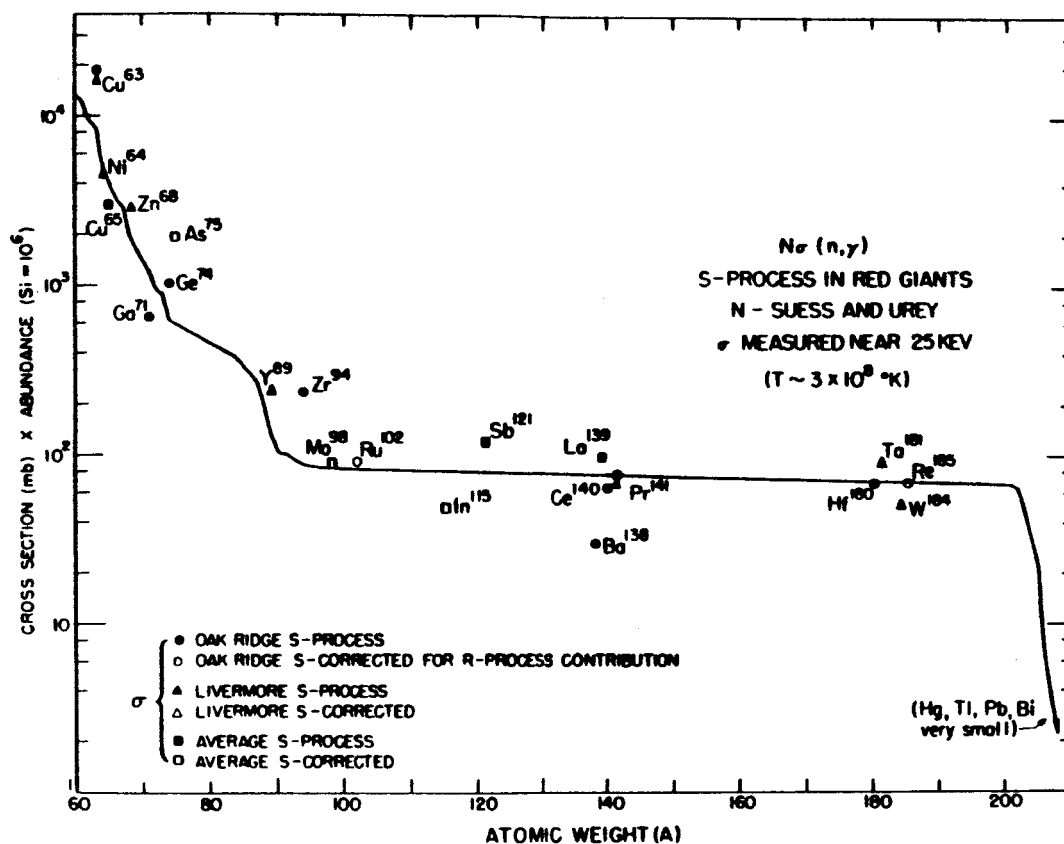
Fig. 2. A superposition of exposures to approximately fit the observed $\sigma N$ data curve: $\sigma_A N_A = 2160 \, \psi(n_c = 2.8) + 990 \, \psi(n_c = 6.9) + 45 \, \psi(n_c = 34) + 45 \, \psi(n_c = 100)$. This figure is taken from Clayton et al. (1961).

45 $\psi(n_c = 34) + 45 \psi(n_c = 100)$. For example, the second and third terms on the right-hand side of this equation indicate that for 6.9 average neutron captures by 990 $Fe^{56}$ atoms, 34 average neutron captures have occurred for 45 $Fe^{56}$ atoms. W. A. Fowler (1964) has pointed out that the experimental evidence of this work tends to vertify the theory that $Fe^{56}$ seed nuclei have been subjected to discrete neutron exposures. Clayton (1964) has found another precipitous drop in the $\sigma N$ curve beginning at $A \approx 137$, with the $\sigma N$ curve from $A = 140$ to $A = 200$ being lowered by a factor of $\sim 10$ compared with the same mass range as shown in Fig. 2. The modified $\sigma N$ curve, with the tenfold drop from $A = 140$ to $200$, has been calculated by Clayton (1964) after the analysis of Clayton et al. (1961); the important change concerned the last term in the equation above--namely, 3.6 instead of 45 $Fe^{56}$ seed nuclei absorbed 100 neutrons.

## Cosmochemical behavior of Zr in meteoritic and terrestrial matter

Atomic abundances of Zr decrease steadily from 32 ± 3, 23 ± 3, and 20 ± 3 in the three classes of carbonaceous chondrites, with no significant difference between Types II and III. For seventeen "ordinary" H- and L-group chondrites, the $Zr/10^6$ Si atomic ratio is 16 ± 5. No Zr abundance differences exist within experimental error between "ordinary" chondrites and the LL-group or Soko-Banjites (amphoterites).

Zirconium abundances in Type II and Type III carbonaceous chondrites are enriched to the same degree, 35%, compared with "ordinary" chondrites as are the fourteen rare-earth elements (REE) and yttrium and scandium. Other lithophilic trace elements such as Ba and U (Reed et al., 1960) exhibit enrichment trends in the carbonaceous chondrites, although the sparse data limit the certainty of the trends. Since the chemical properties are sufficiently different for Zr, fourteen REE, Y, Sc, Ba, and U, the general enrichment of these lithophilic trace elements in Type II and Type III carbonaceous chondrites compared with "ordinary" chondrites may hardly be interpreted in terms of diadochic replacement. The enrichment by orders

of magnitude of elements such as Cd, Pb, Bi, Tl, Te, and I in carbonaceous compared with "ordinary" chondrites (Urey, 1964) has been ascribed generally to the chalcophilic property of these elements. Furthermore, it is not clear what precise physicochemical mechanism may be responsible for enrichment of these chalcophilic elements.

Conversely, the observed enrichment (~35%) relative to Si of the lithophilic elements in carbonaceous chondrites may be expressed as a loss or depletion of Si in carbonaceous chondrites compared with ordinary chondrites. Indeed, Mason (1962-1963) has shown that the Si percentage in the three types of carbonaceous chondrites varies uniformly from 10 to 15%, compared with 18% in ordinary chondrites. Urey (1964) has pointed out that variations of even macro-abundant chemical elements in carbonaceous and ordinary chondrites are still not understood; therefore, explanations for trace elemental differences may be premature. Any meaningful interpretation of those enrichments must await abundance determinations of these trace elements in the various separated meteoritic minerals, such as olivine, pyroxenes, etc.

Zr abundances in four Ca-rich achondrites (~5% of all observed meteoritic falls) are about five times greater compared with "ordinary" chondrites. Again, this fivefold enhancement is in line with about tenfold enrichments of other trace elements such as Ba, the fourteen REE, Y, Th, and U in this subclass of achondrites. If some parental chondritic matter were melted with segregation of metallic iron-nickel, trace elements with large ionic radii would be found in the "slag" or residual Ca-rich achondritic matter. Differences in enrichment could certainly be attributed to melting points of the host minerals and the over-all chemical composition and cooling temperatures. Too few Ca-poor achondrites and pallasitic olivines have been analyzed and the uncertainty of their Zr abundances discourages any abundance interpretation. However, it may be cautiously noted that the low Zr abundances are not inconsistent with a model (Ringwood, 1961) wherein the Ca-poor achondrites are one of the fractionation products of

melted and differentiated parental chondritic matter. With enrichment of Zr in Ca-rich achondrites, a depletion should evidently be observed in Ca-poor achondrites.

Finally, Table 7 clearly demonstrates that Zr and Hf have not been fractionated relative to chondritic meteorites in formation of the terrestrial crust. The Zr/Hf atomic abundance of 100 of this work was calculated using the atomic Hf abundance of 0.16, that found by Setser and Ehmann (1964)--see above for discussion of their Hf reliability. This pair of elements--always found together--should have been fractionated least in crustal formation than any other pair of elements (Goldschmidt, 1954). In terrestrial zircon, Hf never exceeds ~0.1 of the Zr abundance (Goldschmidt, 1954; Kosterin et al., 1958). The same valency and almost identical ionic radii dictate chemical similarity.

Table 7

ATOMIC ABUNDANCES OF Zr AND Hf IN METEORITIC
AND TERRESTRIAL MATTER PER $10^6$ Si ATOMS

|  | $Zr/10^6$ Si | $Hf/10^6$ Si | Zr atoms/Hf atoms |
|---|---|---|---|
| Ordinary chondrites | $16$[a] | $0.16$[b] | 100 |
| Terrestrial crust | $180$[c] | $1.7$[d] | 106 |

[a]This work, for 17 ordinary chondrites.

[b]Ehmann and Setser (1963), and Setser and Ehmann (1964).

[c]Taylor (1964) calculates crustal average at equal parts of basalt and granite.

[d]Taylor (1964) calculates Hf by using Zr atoms/Hf atoms ratios, in zircons, of 147 in basic rocks and 88 in granites. These atomic ratios correspond to 75 and 45, respectively, for weight ratios.

# APPENDIX

## A. EMISSION SPECTROGRAPHIC PROCEDURE

Samples were crushed in a hardened-steel diamond mortar and ground in a Wig-L-Bug vial. Obvious pieces of metal which remained after the grinding process were removed from the sample.

The analysis for zirconium was based on a working curve constructed from two different series of standards. The first series consisted of dilutions of a mixture of zirconium dioxide in a quartz-feldspar base (6 quartz/4 feldspar). The second series consisted of dilutions of the standard graphite (G-1) and standard diabase (W-1) (Fairbairn et al., 1951). The value used for G-1 was 210 ppm and for W-1 was 100 ppm (Stevens et al., 1960).

Each standard and sample was mixed in the proportion of 2:2:1 with a base containing 10% sodium carbonate in quartz and with graphite. The purpose of the 10% sodium carbonate in quartz is to make the sample more like the rock standards in their arcing characteristics. The graphite serves to smooth the burn and prevent the formation of a refractory bead which might be expelled from the electrode. Loss of the refractory bead would give abnormally low values for zirconium as it is concentrated in this portion of the burn.

The samples and standards were exposed at least twice and the analytical line Zr 3273.05 was used. The following equipment and technique was used:

Spectrograph:     Jarrell-Ash 3.4-meter grating instrument,
                  Wadsworth mount, dispersion 5.2 A/mm in the
                  first order.

Excitation:       19 ampere short-circuit d-c arc from a Jarrell-
                  Ash Varisource. Sample as the anode. Analytical

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gap 4 mm, magnified 2× and focussed on a 4-mm aperture; vertical cylindrical lens focusses this aperture on the spectrograph slit. The central 2 mm is used with a slit width of 25 microns and a two-step filter. 25 mg samples are arced to completion (120 seconds). The total energy method is used with no internal standard.

Electrodes:    High-purity 1/4-in. graphite electrodes, U.C.C. No. 3417, as the anode. Pointed 1/8-in. cathode.

Plates:    Eastman Kodak III-O.

Processing:    4 minutes in KD-50 developer at $20^\circ$C; 20-second short stop; 10-minute acid fix; 20-minute wash.

Calibration:    Selected iron lines after the method of Dieke and Crosswhite (1943). Each plate is calibrated.

Microphotometer:    Jarrell-Ash Model 2100.

Analytical line:    Zr 3273.05.

The concentration of zirconium in chondrites lies very close to the limit of sensitivity, and standards were therefore exposed on each plate. Sensitivity varied from one emulsion batch to another. Figure 3 is a composite working curve. Note the poor slope for low values of zirconium.

## B. RADIOCHEMICAL PROCEDURE FOR DETERMINATION OF THE ABUNDANCES OF Zr AND Hf BY NEUTRON ACTIVATION ANALYSIS

### Sample preparation and irradiation

A sample is crushed in a hardened-steel diamond mortar that is reserved for meteorite analyses. The 1- to 2-g specimen is weighed on an analytical balance in a tared, clean, 2-dram polyethylene vial. Zr and Hf standards of 2-ml volume are pipetted into 2-dram polyethylene vials
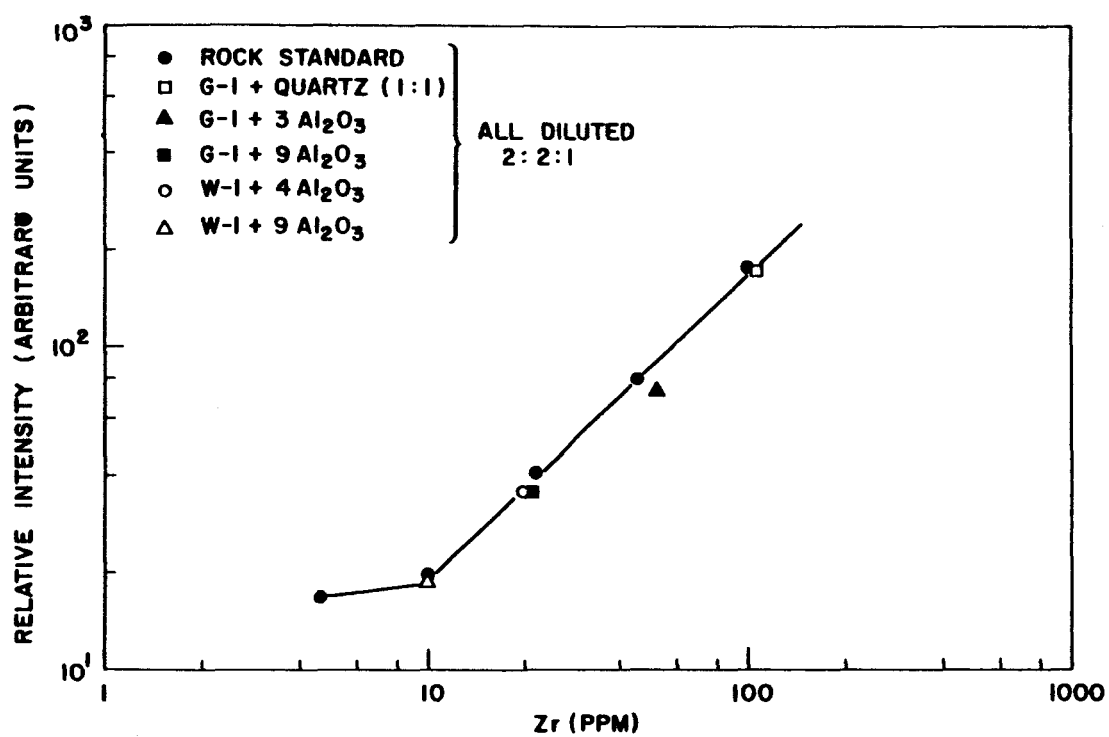
Fig. 3. Composite working curve for emission spectroscopic analysis of Zr via line 3273. 05. All standard mixtures were diluted at 2:2:1 (see Appendix).

which are subsequently heat-sealed. Meteorite specimens and standards are then placed in separate polystyrene irradiation capsules and inserted into the rotary specimen rack of the TRIGA reactor. Irradiations normally consist of 2 hours at a thermal-neutron flux of $2 \times 10^{12}$ $cm^{-2}$ $sec^{-1}$. Rotation of the rotary rack at 1 rpm ensures a uniform neutron flux through the meteoritic sample and standards. Approximate amounts of Zr and Hf standards are about 200 and 10 $\mu$g, respectively.

## Preparation of Zr and Hf carriers and standards

The Zr carrier solution was prepared by dissolving 8.2 g of $Zr(NO_3)_4$, (Jarrell-Ash No. 2171, 2% Hf) in 1$\underline{N}$ $HNO_3$-Hf and diluting to 450 ml in a polyethylene bottle. Zr reference standard solution was prepared by pipetting 10.0 ml of the Zr carrier solution and diluting to 500 ml with a solution that was 1$\underline{N}$ in $HNO_3$ and contained 1 ml HF.

Hf carrier preparation consisted in first dissolving 5.31 g of Hf sponge (United Mineral and Chem. Corp., Lot 259-F-1, reactor grade, 2.6% Zr) in dilute $HNO_3$ and HF and diluting to 500 ml with a solution that was 1$\underline{N}$ in $HNO_3$-HF and designated Hf "A" solution. The final Hf carrier solution was made by diluting 250 ml of the Hf "A" solution to 500 ml with 1$\underline{N}$ in $HNO_3$ and HF. The Hf reference standard was prepared by first pipetting 10 ml of Hf "A" into a volumetric flask and diluting to 1000 ml in 1$\underline{N}$ $HNO_3$ and labelled Hf "B". The final Hf reference standard was made by diluting 25.0 ml of Hf "B" to 500-ml volume, 1$\underline{N}$ in $HNO_3$ and HF.

Both Zr and Hf carrier solutions were standardized via the p-bromomandelic method (Hahn, 1951) and found to be 4.97 mg Zr/ml and 5.21 mg Hf/ml.

Two milliliters each of Zr and Hf carrier were pipetted into a test tube. Precipitation of the hydroxides by addition of concentrated $NH_4OH$ was quantitative, followed by addition of some paper pulp. After filtration of the hydroxides on ashless No. 42 filter paper, the paper and precipitates were transferred to a clean 100-ml nickel crucible. After the paper and

precipitate were sufficiently dried, the final ashing to $ZrO_2$ and $HfO_2$ was completed in a muffle furnace at $550^{\circ}C$. These oxides are then mixed with irradiated samples (see below) to serve as carriers.

## Separation steps[*]

1. After neutron irradiation, the meteorite sample is normally set aside for about 8 hr for decay of short-lived radionuclides. An 8-hr wait results in radiation intensities (from a 1-g stone meteorite) of about 1000 milliroentgens per hour (mr/hr) on contact, and about 2 mr/hr at a distance of about 30 cm. Meteoritic sample and reference standard containers are opened with tongs, and all operations are carried out in filtered chemical hoods and behind 2- to 4-in.-thick lead shields.

2. About 1 g of $Na_2O_2$ is added to cover the $ZrO_2$ and $HfO_2$ (carrier oxides), and then the irradiated specimen is added. More $Na_2O_2$ is added to cover the specimen so that the ratio of $Na_2O_2$ to specimen weight is about 5. The mixture is carefully heated over a Meeker burner until molten, and then is kept molten for ~10 min more to ensure complete exchange between the Zr and Hf carriers and the fused Zr and Hf radionuclides. The $Na_2O_2$ fusion method has been used by Travers (1919) and Holladay (1929) for dissolution of zirconium minerals.

3. About 50 ml of $H_2O$ and 50 ml of 12$\underline{N}$ HCl are added to a large beaker containing the nickel crucible (heating the acid solution helps the dissolution of the fusion). The addition of 12$\underline{N}$ HCl with appropriate policing of the crucible removes most of the contents. About 5 ml of 48% HF is then added to complex the Zr and Hf as $ZrF_6^=$ and $HfF_6^=$, and the solution is heated to boil off any remaining $H_2O_2$.

4. The mixture is then centrifuged in polyethylene tubes and the supernatant is collected in a polyethylene beaker. The black precipitate is then given two 10-ml $H_2O$ (plus 1 ml HF) washes. The wash supernatants

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[*]The separation procedure is based in part on the following procedures: Flynn, Glendenin, and Steinberg (1960) and Hillebrand and Lundell (1929).

are poured into a beaker. Tracer experiments showed a 9% Zr and Hf retention in the black precipitate after two washes.

5. About 10 mg of yttrium or lanthanum carrier is added to precipitate $YF_3$ and $LaF_3$ and also to coprecipitate barium and strontium fluorides. After centrifuging in tubes, the precipitate is discarded.

6. Step 5 is repeated.

7. About 5 ml of Ba (barium carrier at ~50 mg/ml) is added to the supernatant and stirred. Excess $NH_4OH$ is added to precipitate the hydroxides, which are centrifuged. The precipitate is washed with ~50 ml $H_2O$.

8. Two ml of 15$\underline{N}$ $HNO_3$ and ~20 ml $H_2O$ are added to dissolve the precipitate. Also, 2 ml HF and 2 ml Ba carrier are added. The mixture is centrifuged with Zr and Hf in the white precipitate.

9. The white precipitate is washed with 10 ml $H_2O$ and 1 ml Hf. (About 60% of the Zr and Hf are in the precipitate.)

10. After the fluorinated precipitate is dissolved by the addition of 4 ml saturated (sat.) $H_3BO_3$ and 2 ml 15$\underline{N}$ $HNO_3$, the solution is diluted to 10 ml. If some precipitate remains, the mixture is centrifuged and the precipitate washed with 1 ml sat. $H_3BO_3$ and 0.5 ml 15$\underline{N}$ $HNO_3$. Washings are combined with the first dissolved supernatant.

11. $Ba(Zr, Hf)F_6$ is precipitated by adding 2 ml HF and 2 ml Ba to the supernatant. The supernatant is discarded after centrifugation. One $H_2O$ wash is sufficient.

12. The precipitate is dissolved in 2 ml sat. $H_3BO_3$ and 1 ml $HNO_3$ and diluted to 10 ml. Two ml of Ba and 2 ml HF again precipitate $Ba(Zr, Hf)F_6$. The precipitate is quite bulky owing to the coprecipitation of other fluorides, such as $CaF_2$. After centrifuging, the supernatant is discarded and the precipitate is washed once with 10 ml $H_2O$.

13. $Ba(Zr, Hf)F_6$ and other coprecipitated insoluble fluorides are dissolved in 2 ml sat. $H_3BO_3$ and 2 ml 12$\underline{N}$ HCl and diluted to 10 ml. Excess $NH_4OH$ is added to precipitate the hydroxides, which are centrifuged and decanted.

14. The hydroxides are dissolved in 3 ml 15$\underline{N}$ $HNO_3$, diluted to 10 ml,

heated to boiling, and then kept hot for ~20 min. The solution is poured into a separatory funnel containing 30 ml $0.4\underline{N}$ TTA (thenoyltrifluoroacetone) in benzene. After a 20-min thorough shaking, the aqueous phases are discarded.

15. Two 10-ml $1\underline{N}$ $HNO_3$ scrubbings of 2 min each are performed.

16. 15 ml $H_2O$ plus 2 ml HF are shaken for 3 min to extract the Zr and Hf from the TTA. About 2 ml Ba and 1 ml $HNO_3$ precipitate $Ba(Zr,Hf)F_6$ from the aqueous phase. After centrifuging, the precipitate is washed with 10 ml $H_2O$.

17. The precipitate is dissolved in 1 ml sat. $H_3BO_3$ and 0.5 ml $15\underline{N}$ $HNO_3$ and diluted to 10 ml $H_2O$. Again, $Ba(Zr,Hf)F_6$ is precipitated by the addition of 1 ml Ba and 1 ml HF followed by centrifugation.

18. The precipitate is dissolved in 1 ml sat. $H_3BO_3$ and 2 ml $12\underline{N}$ HCl and diluted to 10 ml. Two drops of $36\underline{N}$ $H_2SO_4$ are added to precipitate $BaSO_4$, which is heated to boiling before centrifugation.

19. Excess $NH_4OH$ is added to precipitate the Zr and Hf hydroxides, followed by centrifugation and a 10 ml $H_2O$ wash.

20. The precipitates are dissolved in 2 ml $6\underline{N}$ HCl, and the solution is passed through a $6\underline{N}$ HCl equilibrated 3 ml AG 1 × 10, 200 to 400 mesh, anion exchange column; a flow rate of <1 cm/min is maintained. Another column volume of $6\underline{N}$ HCl is then passed through the column.

21. Excess $NH_4OH$ is added to the combined eluants to precipitate the hydroxides. After centrifugation and a 10-ml $H_2O$ wash, the precipitate is dissolved in 1 ml $HNO_3$ and diluted to 10 ml. Another $NH_4OH$ precipitation, centrifugation, and 10-ml $H_2O$ wash is performed.

22. The precipitate is dissolved in minimum HCl and poured into a 2-dram polyethylene vial; it is then diluted to 4-ml volume and heat-sealed and labeled.

23. The irradiated Zr and Hf reference standards are poured into separate 2-dram, polyethylene vials, diluted to 4-ml volume, and heat-sealed.

24. The decay of the Hf and Zr standards and the labeled Hf-Zr sample are followed in a lead-shielded 1-3/4-in. by 2-in. NaI(Tl) well-type scintillation gamma-ray single-channel spectrometer. The decay of the 443-keV gamma ray of 5.5-hr $Hf^{180m}$ and the 665-keV and 747-keV gamma rays of 17-hr $Zr^{97} \rightarrow$ 60-sec $Nb^{97m}$, 72-min $Nb^{97}$ (in equilibrium) are followed in appropriate windows. Any long-lived components are subtracted first in order to analyze the 17-hr decay equilibrium curve.

25. Chemical yields of Hf and Zr are determined by neutron irradiation (for ~10 min at $2 \times 10^{12}$ $cm^{-2}$ $sec^{-1}$) of the decayed Hf-Zr sample and a 2-dram polyethylene vial containing 2.0 ml each of Hf and Zr carriers. Direct comparison of the induced 42-d $Hf^{181}$ (480 keV) peak heights taken by a multichannel gamma-ray spectrometer yields the radiochemical recovery factor (chemical yield).

From the chemical yields and decay data, the abundances of Hf and Zr are determined.

The determination of the chemical yield rests on the assumption that the Zr/Hf ratio remained unchanged throughout the radiochemical procedure. In the radiochemical procedure, the only possible Zr-Hf fractionation could have occurred during step 14, namely in the extraction of Zr and Hf into 0.4$\underline{M}$ TTA in benzene. Huffmann and Beaufait (1949) reported Zr-Hf separation using 0.025$\underline{M}$ TTA in benzene from a 2$\underline{N}$ $HClO_4$ solution. Ehmann and Setser (1964) and Setser (1963) observed that virtually all the Zr and 50% of the Hf were extracted under the above conditions. Using 0.4$\underline{M}$ TTA (as in this work) instead of 0.025$\underline{M}$ TTA should reduce the Zr selectivity relative to Hf to negligible proportions. Even if some Zr were preferentially extracted into the 0.4$\underline{M}$ TTA relative to Hf, the recovered quantity of Hf would be decreased. Subsequent activation (Step 25) of the decayed Zr-Hf sample would yield a lower chemical recovery. Therefore, the calculated Zr abundances will always be high values; i.e., if 10% less Hf compared to Zr were extracted into the 0.4$\underline{M}$ TTA, all the true Zr abundances will be less by 10% than the calculated ones.

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The entire procedure was checked by using radioactive tracers 65-d $Zr^{95}$ and 43-d $Hf^{181}$. Two milliliters each of Zr and Hf carrier ($\sim$10 mg Zr and $\sim$10 mg Hf) were irradiated in the TRIGA reactor for $\sim$1 hr at $2 \times 10^{12}$ neutrons $cm^{-2}$ $sec^{-1}$ before conversion to $ZrO_2$ and $HfO_2$. Sufficient time elapsed for the decay of 17-hr $Zr^{97}$ and 5.5-hr $Hf^{180m}$.

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